

Protonation Enthalpies in Fluorosulfonic Acid Using *Ab Initio* Self-Consistent Reaction Field Theory

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ABSTRACT: Electrostatic solvation free energies were computed for several small neutral bases and their conjugate acids using a continuum solvation model called the self-consistent isodensity polarizable continuum model (SCIPCM). The solvation energies were computed at the restricted Hartree–Fock (RHF) and second-order Møller–Plesset (MP2) levels of theory, as well as with the Becke3–Lee–Yang–Parr (B3LYP) density functional theory, using the standard 6–31G** Gaussian basis set. The RHF solvation energies are similar to those computed at the correlated MP2 and B3LYP theoretical levels. A model for computing protonation enthalpies for neutral bases in fluorosulfonic acid solvent leads to the equation $\Delta H_{\text{prot, HSO}_3\text{F}}(\text{B}) = -\text{PA}(\text{B}) + \Delta E_{\text{t}}(\text{BH}^+) - \Delta E_{\text{t}}(\text{B}) + \beta$, where $\text{PA}(\text{B})$ is the gas phase proton affinity for base B, $\Delta E_{\text{t}}(\text{BH}^+)$ is the SCIPCM solvation energy for the conjugate acid, and $\Delta E_{\text{t}}(\text{B})$ is the solvation energy for the base. A fit to experimental values of $\Delta H_{\text{prot, HSO}_3\text{F}}(\text{B})$ for 10 neutral bases (H_2O , MeOH , Me_2O , H_2S , MeSH , Me_2S , NH_3 , MeNH_2 , Me_2NH , and PH_3) gives $\beta = 238.4 \pm 2.9$ kcal/mol when $\Delta \Delta E_{\text{t}}$ is computed using the $0.0004 \text{ e} \cdot \text{bohr}^{-3}$ isodensity surface for defining the solute cavity at the RHF/6–31G** level. The model predicts that for carbon monoxide $\Delta H_{\text{prot, HSO}_3\text{F}}(\text{CO}) = 10$ kcal/mol. Thus, protonation of CO is endothermic, and the conjugate acid HCO^+ (formyl cation) behaves as a strong acid in fluorosulfonic acid. © 1998 John Wiley & Sons, Inc. *J Comput Chem* **19**: 250–257, 1998

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Introduction

The relation between gas phase and solution phase acidity is of longstanding interest in physical organic chemistry.^{1,2} Gas phase acidities are computed very accurately by high level *ab initio* theory for small molecules.^{2a} Ion solvation energies can now be computed by *ab initio* theory, which allows computation of acidities in solution.²

Here we compute theoretical solvation energies using a polarizable continuum solvation model (PCM).³ We develop a simple empirical model for finding the enthalpies for protonation of weak neutral bases in a superacid solvent (fluorosulfonic acid). This work has implications for electrophilic reactions such as sulfonations, acylations, and nitrations.⁴ We are interested in understanding the solvent effects on the energies of reactants, products, and intermediates in such reactions.

HSO₃F is a powerful acid, with $H_o = -15.1$ on the Hammett acidity scale.⁵ The protonating power is increased several orders of magnitude (to $H_o < -25$) in mixtures of HSO₃F with the Lewis superacid SbF₅. Arnett and coworkers measured solvation enthalpies for a number of strong bases in HSO₃F.¹ Water, for example, is a strong base that is completely protonated in HSO₃F. This available experimental data was used to test our theoretical model.

The enthalpy changes for gas phase and solution phase proton transfers are related as shown in Scheme 1. In Scheme 1 ΔPA is the difference in proton affinities for A[−] and B. $\Delta H_t(X)$ is the enthalpy for transfer of species X from the gas phase to solution. The proton transfer enthalpy in solution is

$$\Delta H_{\text{prot},s} = \Delta PA + \Delta \Delta H_t(B, BH^+) - \Delta \Delta H_t(A^-, AH), \quad (1)$$

where $\Delta \Delta H_t(B, BH^+) = \Delta H_t(BH^+) - \Delta H_t(B)$.

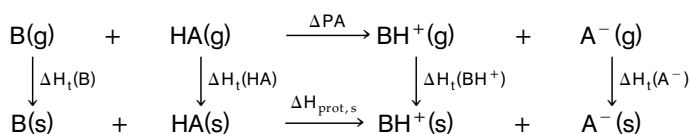
When a neutral base and neutral acid react to give ionic products, the contribution from the $\Delta \Delta H_t$ terms is large and exothermic while ΔPA is large and endothermic. The resulting $\Delta H_{\text{prot},s}$ can

be endothermic or exothermic, depending on the difference of the two large quantities. The reaction between ammonia and fluorosulfonic acid gives an illustration of the effect of solvation on proton transfer equilibria. Ammonia is a strong neutral base [$PA(NH_3) = 204.0$ kcal/mol],⁵ and fluorosulfonic acid is a strong neutral acid [$PA(SO_3F^-) = 307$ kcal/mol],⁶ but the gas phase proton transfer is endothermic by $\Delta PA = 103$ kcal/mol. The enthalpy change for the same proton transfer in fluorosulfonic acid solvent is highly exothermic by $\Delta H_{\text{prot},\text{HSO}_3\text{F}} = -43$ kcal/mol.¹ Thus, the separation of charge is favored in a polar medium but not in the gas phase.

The solvent is described in the PCM as a continuous polar medium.² This is a different approach from microscopic solvation models⁸ that describe interactions between the solute and solvent explicitly. One might expect the microscopic models to perform better than continuum models when the solute–solvent interface is highly structured, as in hydrogen bonded systems. Even so, the continuum model has proved useful for computing ion solvation enthalpies in water.⁹

Methods

In continuum solvation models^{3,9,10} the solute is embedded in a cavity surrounded by a solvent dielectric. The simplest models use a spherical or elliptical cavity. More sophisticated models use an irregularly shaped cavity defined with atom centered spheres. An important concept in the continuum models is the *reaction field*,^{3b} which is the electric field induced in the continuum by the charge distribution of the solute. In *self-consistent reaction field* (SCRF) theory,¹⁰ the solute charge distribution is allowed to be polarized by the reaction field and the calculation is iterated until self-consistency is achieved. The PCM³ and other versions of SCRF theory are quantum mechanical approaches in which the electrostatic potential is included in the molecular Hamiltonian operator. In classical continuum solvation models⁹ the charge distribution of the solute is represented by point charges (sometimes dipoles and higher mul-



SCHEME 1. The enthalpy changes for gas phase and solution phase proton transfers.

tipoles are included) located at the atomic nuclei. This is more suitable than the quantum approach for large systems such as peptides or polynucleotides.

Calculations were carried out on IBM RISC/6000 (3BT) workstations using the Gaussian 94 suite of *ab initio* programs.¹¹ The restricted Hartree-Fock (RHF),¹² second-order Møller-Plesset (MP2),¹² and nonlocal Becke3-Lee-Yang-Parr (B3LYP) density functional¹³ theories were employed, using the 6-31G* and 6-31G** basis sets of Gaussian functions.¹² These theories and basis sets are standard in Gaussian 94. Geometries for H₂O, MeOH, Me₂O, NH₃, MeNH₂, Me₂NH, H₂S, MeSH, Me₂S, and PH₃ were optimized at the RHF/6-31G*, MP2/6-31G*, and B3LYP/6-31G* theoretical levels. The geometries for the corresponding cationic conjugate acids were also optimized. Single point gas phase and solution phase SCRF energies were then computed at the RHF/6-31G**, MP2/6-31G**, and B3LYP/6-31G** levels. For example, the SCRF solution phase energies for H₂O and its conjugate acid H₃O⁺ were computed at the B3LYP/6-31G** level while keeping the structures fixed at the B3LYP/6-31G* gas phase minima.

We use a modification of Tomasi's PCM,^{3a} called the self-consistent isodensity surface polarizable continuum model (SCIPCM).^{3c} The SCIPCM is standard in Gaussian 94. In the SCIPCM the boundary between the solute and the solvent is described by a surface of constant electron density.^{3c} This differs from the PCM, which defines the cavity using atom centered spheres with fixed radii.^{3a} The solvent continuum surrounds the isodensity surface that defines the solute cavity. The SCIPCM describes the electrostatic interaction between the solute and solvent, but it does not describe nonelectrostatic interactions that also contribute to the solvation energy.^{9,10,14}

The only special parameters needed for the Gaussian 94 implementation of the SCIPCM are the solvent dielectric constant (ϵ) and the electron density contour level (ρ_o) for defining the isodensity surface. The dielectric constant was fixed at $\epsilon = 120$, the value for fluorosulfonic acid.⁵ The dielectric constant is expected to vary with temperature, but the solvation energy is quite insensitive to changes in the dielectric. [This is expected from the simple Born model^{9b,14} in which the ion solvation energy is a function of $(1 - 1/\epsilon)$.] The electrostatic solvation energy depends rather strongly on ρ_o , becoming larger as the solute cavity is made smaller (i.e., as ρ_o is made larger, see

Fig. 1). A previous study showed $\rho_o = 0.0004 \text{ e} \cdot \text{bohr}^{-3}$ is the best contour level for reproducing experimental molar volumes for a set of small organic solutes.¹⁵ The solvation energy was computed using two different contour levels, $\rho_o = 0.0004$ (method A) and $\rho_o = 0.001 \text{ e} \cdot \text{bohr}^{-3}$ (method B).

Results and Discussion

SOLVATION ENERGIES

The SCIPCM electrostatic solvation free energies $\Delta E_t(\text{B})$ for 10 neutral bases and the solvation energies $\Delta E_t(\text{BH}^+)$ for the corresponding 10 conjugate acids are presented in Table I. The notation ΔE_t indicates the energy change for transfer from the gas phase to solution, computed from $\Delta E_t = E_s - E_g$, where E_s is the solution phase SCRF energy and E_g is the gas phase energy.

Comparison of the RHF, B3LYP, and MP2 solvation energies shows the energies are nearly independent of the level of theory.^{3c} However, the RHF solvation energies tend to be larger by 0.3–0.5 kcal/mol than the MP2 or B3LYP energies. It appears that the RHF theoretical level is satisfactory, so the extra computational cost of SCIPCM computations at the higher theoretical levels is not necessary. In the case for Me₂SH⁺, the MP2 calculation did not converge at the higher contour level of $0.001 \text{ e} \cdot \text{bohr}^{-3}$.

Increasing the contour level from 0.0004 to $0.001 \text{ e} \cdot \text{bohr}^{-3}$ leads to the expected uniform increase in computed solvation energies. The average increase is $1.2 \pm 0.5 \text{ kcal/mol}$ for the neutral bases and $12.6 \pm 0.7 \text{ kcal/mol}$ for the monopositive conjugate acids. It seems that changing the contour level has a fairly uniform effect on the solvation energies, so that differences $\Delta\Delta E_t$ for pairs of bases and pairs of conjugate acids are nearly independent of the choice of contour level. The insensitivity of $\Delta\Delta E_t$ to contour level is illustrated in Figure 1 for the three ammonium ions NH₄⁺, MeNH₃⁺, and Me₂NH₂⁺. The RHF/6-31G** solvation energies are plotted against $\log(\rho_o)$, over the range $\rho_o = 0.00001\text{--}0.0025 \text{ e} \cdot \text{bohr}^{-3}$. The curves for the three ions are parallel except at the highest contour levels. The errant behavior at large ρ_o is probably caused by leakage of charge density outside of the solute cavity.^{3a}

Inspection of ΔE_t values for the three series of neutral bases (amines, oxides, and sulfides) reveals a clear trend on solvation energies related to methyl

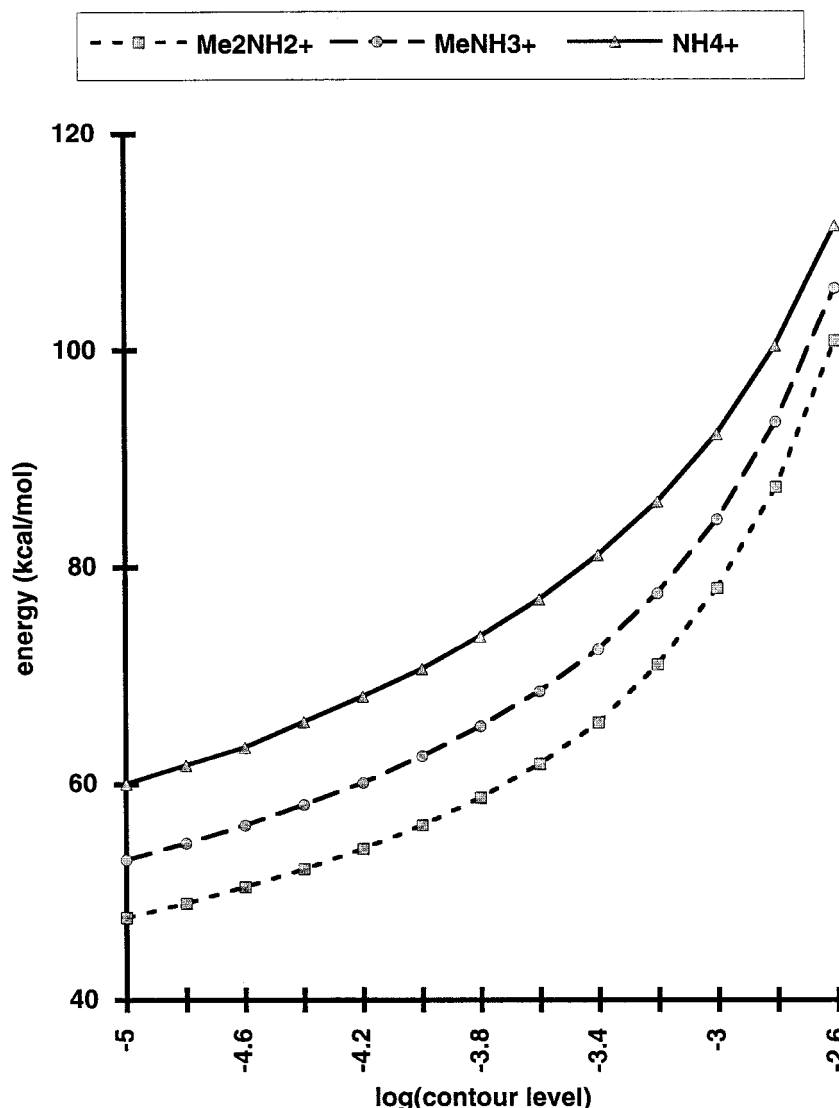


FIGURE 1. Plot of RHF/6-31G** solvation energy (kcal/mol) vs. $\log(\rho_0)$ for NH_4^+ , MeNH_3^+ , and Me_2NH_2^+ .

substitution.¹⁴ In every case methyl substitution leads to a decrease in the electrostatic solvation energy. For the amines substitution of methyl for hydrogen causes a decrease of 0.9 kcal/mol for each replacement (Table I, B3LYP/A). In the oxides each substitution causes a decrease of 1.8 kcal/mol. In the sulfides the effect is an order of magnitude smaller; each methyl substitution changes the solvation energy by 0.04 kcal/mol. The same trend is seen in the three series of cations (i.e., the ammonium, oxonium, and sulfonium ions in Table I). In the ammonium ions the first and second methyl substitutions lead to respective decreases of 8.4 and 6.7 kcal/mol in ΔE_t .^{9c,9d} In the oxonium ions the decreases are

14.9 and 10.9 kcal/mol, and in the sulfonium ions the decreases are 7.8 and 5.7 kcal/mol for replacement of H by CH_3 (Table I, B3LYP/A).

Some comparisons of SCIPCM energies with available experimental data for aqueous solvation of amines¹⁴ and ammonium ions^{9c} are presented in Table II. The experimental solvation enthalpies for the anionium ions rely on a thermochemical cycle similar to Scheme 1, using a solvation enthalpy $\Delta H_t(\text{H}^+) = -262.2$ kcal/mol for the proton.^{9b} The SCIPCM $\Delta E_t(\text{BH}^+)$ values computed at $\rho_0 = 0.0004$ are, respectively, 81.1, 72.5, and 65.8 kcal/mol for NH_4^+ , MeNH_3^+ , and Me_2NH_2^+ . These are larger than the corresponding experimental transfer enthalpies by ca. 4 kcal/mol. On the other

TABLE I.
SCIPCM Electrostatic Solvation Free Energies (kcal / mol) for Neutral Bases and Their Conjugate Acids.

	RHF / A	RHF / B	B3LYP / A	B3LYP / B	MP2 / A	MP2 / B
Neutral Bases						
NH ₃	3.72	5.34	3.47	4.99	3.57	5.14
MeNH ₂	2.82	4.15	2.57	3.81	2.70	3.99
Me ₂ NH	2.00	3.04	1.76	2.73	1.91	2.94
H ₂ O	6.19	8.69	5.29	7.54	5.68	8.05
MeOH	4.26	6.04	3.48	5.17	3.82	5.53
Me ₂ O	2.19	3.20	1.76	2.63	1.94	2.87
H ₂ S	1.92	3.09	1.91	3.06	1.83	2.95
MeSH	2.00	3.11	1.88	2.93	1.78	2.80
Me ₂ S	2.04	3.12	1.84	2.81	1.74	2.71
PH ₃	0.81	1.39	0.72	1.23	0.73	1.26
Monopositive conjugate acids						
NH ₄ ⁺	81.12	92.21	80.53	91.73	80.39	91.57
MeNH ₃ ⁺	72.49	84.35	72.10	84.13	72.04	84.02
Me ₂ NH ₂ ⁺	65.76	78.04	65.43	77.78	65.39	77.72
H ₃ O ⁺	93.89	106.30	92.33	104.72	92.71	105.17
MeOH ₂ ⁺	77.83	90.17	77.40	90.07	77.60	90.33
Me ₂ OH ⁺	66.88	79.05	66.54	79.08	66.54	79.29
H ₃ S ⁺	74.46	88.33	74.37	88.10	74.04	87.98
MeSH ₂ ⁺	66.88	80.58	66.64	80.27	66.63	80.41
Me ₂ SH ⁺	61.29	74.93	60.94	73.96	61.06	—
PH ₄ ⁺	71.14	83.72	70.48	82.88	70.62	83.24

Method A: 6-31G** basis, $\rho_o = 0.0004 \text{ e} \cdot \text{bohr}^{-3}$. Method B: 6-31G** basis, $\rho_o = 0.001 \text{ e} \cdot \text{bohr}^{-3}$. The dielectric is fixed at $\epsilon = 120$ for fluorosulfonic acid. (—) SCIPCM calculation with $\rho_o = 0.001 \text{ e} \cdot \text{bohr}^{-3}$ did not converge.

hand, the $\Delta E_t(B)$ values for NH₃, MeNH₂, and Me₂NH computed at the same contour level are smaller than the experimental $\Delta H_t(B)$ values by 4–11 kcal/mol.

Reproducing the experimental transfer enthalpies is not our goal, but clearly the energies would agree better with a lower contour level for the cations and a higher contour level for the neutral bases. The entropic contributions ($T\Delta S_t$) are similar for B and BH⁺, which suggests that the

difference $\Delta H_{\text{prot,H}_2\text{O}} - \Delta G_{\text{prot,H}_2\text{O}}$ should be fairly constant in a series of similar bases.¹⁴

MODEL FOR COMPUTING PROTON
TRANSFER ENTHALPIES

At this point we turn to calibration of a theoretical model to compute proton transfer enthalpies in fluorosulfonic acid. We make use of the experimental PA values⁸ and the experimental solution

TABLE II.
Comparison of Computed Solvation Energies with Experimental Enthalpies (kcal / mol) for Aqueous Solvation of Amines and Their Conjugate Acids, and Entropic Contributions to Solvation Energy.

Base	$-\Delta E_t(B)^a$	$-\Delta E_t(BH^+)^a$	$-\Delta H_t(B)^b$	$-\Delta H_t(BH^+)^b$	$-T\Delta S_t(B)^c$	$-T\Delta S_t(BH^+)^c$
NH ₃	3.72	81.12	8.4(7.5)	77.2(76.3)	6.0	6.6
MeNH ₂	2.82	72.49	10.8(6.3)	67.9(63.4)	8.1	7.7
Me ₂ NH	2.00	65.76	12.7(7.5)	62.2(57.0)	10.3	8.8

^a ΔE_t are SCIPCM electrostatic solvation energies computed at the RHF / 6-31G** level with $\rho_o = 0.0004 \text{ e} \cdot \text{bohr}^{-3}$.
^b ΔH_t are experimental solvation enthalpies for B (ref. 14) and BH⁺ (ref. 9c). Values in parentheses are corrected for nonelectrostatic contributions to ΔH_t (see ref. 9c).
^c Experimentally derived $T\Delta S_t$ are from ref. 14.

proton transfer enthalpies^{1a} in Table III. Proton affinities were also computed using the accurate *ab initio* G2 method,¹⁶ and these are listed in Table III for comparison with the experimental PAs.

In our simple model we replace the experimental $\Delta\Delta H_t(B, BH^+)$ in eq. (1) by the theoretical $\Delta\Delta E_t(B, BH^+)$, which gives

$$\Delta H_{\text{prot, HSO}_3\text{F}} = \text{PA}(\text{B}) + \Delta\Delta E_t(\text{B}, \text{BH}^+) + \beta, \quad (2)$$

where

$$\beta = [-\Delta\Delta H_t(\text{SO}_3\text{F}^-, \text{HSO}_3\text{F}) - \text{PA}(\text{SO}_3\text{F}^-)] \\ + \Delta\Delta H_t(\text{B}, \text{BH}^+) - \Delta\Delta E_t(\text{B}, \text{BH}^+).$$

This is presumed to have a constant value for any neutral base. The bracketed term is certainly constant, so the real assumption is that the difference $\Delta\Delta H_t(\text{B}, \text{BH}^+) - \Delta\Delta E_t(\text{B}, \text{BH}^+)$ is constant.

Is this a reasonable assumption? First we note that the SCRF energy ΔE_t is defined as the electrostatic contribution to the solvation free energy.^{3a, 3b, 10a} In the simple Born model for ionic solvation, $T\Delta S_t$ is only about 2% of ΔG_t ,¹⁴ so that ΔG_t and ΔH_t for solvation of an ion are very similar.^{9b} (However, the nonelectrostatic contribution to $T\Delta S_t$ is substantial, at least in water.^{9a} The solvation entropy is determined mainly by ordering of the solvent around the solute, which leads to a significant negative $T\Delta S_t$ for aqueous solvation.)

Further consideration of the nonelectrostatic contribution to the solvation enthalpy is needed. Our assumption implies that any nonelectrostatic contribution to the difference in solvation enthalpies $\Delta\Delta H_t(\text{B}, \text{BH}^+)$ can be ignored. Aue et al.¹⁴ noted that the nonelectrostatic cavity^{3b} and dispersion^{3b} contributions to $\Delta\Delta H_t(\text{B}, \text{BH}^+)$ should cancel because B and BH^+ are isoelectronic and have similar size, shape, and electron density. This prediction is supported by enthalpy data for ions and isoelectronic neutrals.^{9c, 9d} For example, the nonpolar contributions to the solvation enthalpies of H₂O and NH₄⁺ are -0.9 kcal/mol,^{9d} and the nonpolar contributions to solvation enthalpies for CH₃OH and MeNH₃⁺ are -4.2 and -4.5 kcal/mol, respectively.^{9d} It seems justifiable to use electrostatic solvation energies in our model in place of solvation enthalpies.

Calibration of the model involves finding the value for β using $\Delta H_{\text{prot, HSO}_3\text{F}}$ and PA(B) from Table III and ΔE_t from Table I. For example, the calculation for NH₃ gives $\beta = -43.3 + 204.0 + 81.1 - 3.7 = 238.1$ kcal/mol (RHF/A method). The average β (RHF/A) for the 10 bases in Table I is 238.4 ± 2.9 kcal/mol. At the 0.001 e · bohr⁻³ contour level (RHF/B method), the average β is 249.6 ± 3.2 kcal/mol. As expected, the choice of contour (i.e., RHF/A method vs. RHF/B method) has little impact on the accuracy of the fit.

Thus, a model is developed using a single fitting parameter for computing proton transfer

TABLE III.
Experimental and Theoretical (G2) Proton Affinities (kcal / mol) and Proton Transfer Enthalpies (kcal / mol) in Fluorosulfonic Acid.

Base	Proton Affinity (PA)		Proton Transfer Enthalpy ($\Delta H_{\text{prot, HSO}_3\text{F}}$)		
	Exp.	G2	Exp.	RHF / A	RHF / B
NH ₃	204.0	204.0	-43.3	-43.0	-41.3
MeNH ₂	214.1	215.4	-46.3	-45.4	-44.7
Me ₂ NH	220.6	222.7	-47.8	-46.0	-46.0
H ₂ O	166.5	164.5	-16.5	-15.8	-14.5
MeOH	181.9	180.3	-17.1	-17.1	-16.4
Me ₂ O	192.1	189.3	-18.2	-18.4	-18.3
H ₂ S	170.2	169.2	-5.3	-4.3	-5.8
MeSH	187.4	185.6	-19.2	-13.9	-15.3
Me ₂ S	200.6	198.6	-18.1	-21.4	-22.8
PH ₃	188.6	187.6	-14.4	-20.5	-21.3
			RMS error	2.9	3.2

^a G2 proton affinity includes a correction of 5 / 2RT (1.5 kcal / mol) for the translational enthalpy of the proton.

^b Experimental values for $\Delta H_{\text{prot, HSO}_3\text{F}}$ are from ref. 1a; theoretical values are calculated with eq. (2). RHF / A and RHF / B methods are the same as in Table I.

enthalpies in HSO_3F . The fitted values for $\Delta H_{\text{prot,HSO}_3\text{F}}$ are given in Table III along with the true values.^{1a} The fit is worst for the three second row bases MeSH , Me_2S , and PH_3 . For the other seven bases the experimental and fitted $\Delta H_{\text{prot,HSO}_3\text{F}}$ values agree to within 2 kcal/mol.

As a check of the model, the protonation enthalpy for acetone was computed. The values for PA, $\Delta E_t(\text{B})$, and $\Delta E_t(\text{BH}^+)$ are, respectively, 196.7,⁶ -4.69, and -65.37 kcal/mol (RHF/A method). (The calculated PA using G2 theory is 194.7 kcal/mol at 298 K.) This gives $\Delta H_{\text{prot,HSO}_3\text{F}}(\text{acetone}) = -19.0$ kcal/mol, compared with the experimental value of -19.1 kcal/mol.^{1e} The model gives good agreement with experiment, although carbonyl bases were not included in the calibration data set.

The model, now, calibrated can be used to estimate protonation enthalpies for weak bases that are not completely protonated in HSO_3F . Any base for which $[\text{PA} - \Delta E_t(\text{BH}^+, \text{RHF/A}) + \Delta E_t(\text{B}, \text{RHF/A})] < 238$ kcal/mol can be considered to be a weak base. For example, carbon monoxide has $\text{PA} = 140.9$ (from G2 theory),^{4e} $\Delta E_t(\text{HCO}^+) = -88.53$, and $\Delta E_t(\text{CO}) = -0.81$ kcal/mol. This gives $\Delta H_{\text{prot,HSO}_3\text{F}}(\text{CO}) = +9.8$ kcal/mol. The protonation is quite endothermic in HSO_3F solution. In the more acidic medium HF/SbF_5 ,⁵ protonation of CO should be nearly thermoneutral.

The formyl cation (HCO^+) is a likely intermediate in superacidic formulations of aromatic molecules and adamantane.^{4c-e} However, HCO^+ has proved to be an elusive species that cannot be observed in solution by ^1H NMR or ^{13}C NMR spectroscopy.^{4d,17} This behavior is expected because of the energetically favorable dissociation, $\text{HCO}^+ \rightarrow \text{H}^+ + \text{CO}$, that is predicted by the solvation model.

Conclusions

The SCIPCM electrostatic solvation free energies are computed adequately at the RHF/6-31G** theoretical level. It is not necessary to resort to more expensive theories that include electron correlation. No attempt was made in this work to reproduce absolute solvation energies for bases or for their conjugate acids; but comparison with available experimental data for aqueous solvation of amines and ammonium ions suggests the SCIPCM energies are quite reasonable, especially

after correcting experimental data for nonelectrostatic contributions to the solvation energy. Importantly, the SCIPCM solvation energies reproduce the expected trend of decreased solvation energy for substitution of X-H by X-CH_3 .¹⁴ Our model for computing enthalpies for protonation of neutral bases in fluorosulfonic acid should give enthalpies accurate to within 5 kcal/mol for second row bases (thioethers and phosphines) and 2 kcal/mol for first row bases (amines, ethers, and carbonyl compounds). The model allows prediction of protonation enthalpies for weak bases (e.g., carbon monoxide) that are incompletely protonated in superacids.

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